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**Hot-melt silicone pressure sensitive adhesive with siloxylated polyether waxes as additives.**

The instant invention pertains to a hot-melt pressure sensitive adhesive composition wherein the composition is comprised of (A) a silicone pressure sensitive adhesive selected from a mixture of (i) a silicone resin and (ii) a silicone fluid or a condensed product of (i) and (ii); the silicone pressure sensitive adhesive exhibiting tackiness and adhesiveness; and (B) from 1 to 20 weight percent, based on the total weight of (i) and (ii), of a siloxylated polyether wax. The instant invention also encompasses method of using the composition, methods of making hot-melt silicone pressure sensitive adhesive-coated substrates and devices made using the composition.

**EP 0 663 431 A2**

A pressure sensitive adhesive (PSA) is a material which adheres to a surface with slight pressure and releases from the surface with negligible transfer of the material to the surface. Silicone PSAs known in the art are typically solvent based adhesives. Solvents employed therein are primarily to reduce the silicone PSA's viscosity to facilitate coating onto the substrate of choice and the solvents are removed after coating.

Hot-melt PSAs are those adhesives, which upon heating, melt to viscosities suitable for coating, but when cooled are generally in a flowless state. The advantages of hot-melt PSAs relative to solvent-based PSAs are known and include safety, environmental and application considerations. Additionally, hot-melt PSAs do not contain solvents which interfere with the addition of other ingredients to the PSA. Silicone PSAs are preferred over other types of PSAs in many applications, especially the medical area. PSAs have been used to bind bandages, sensory monitors and the like to a person's skin. In addition, silicone PSAs have found use in transdermal drug delivery applications which involve the adherence of a drug-containing patch to a patient's skin.

Representative of the prior art are US-A 4,865,920; US-A 5,162,410 and EP-A 0 443 759. These hot-melt compositions have been found to be inadequate for the delivery of hydrophilic drugs from transdermal drug delivery systems. There are several advantages to having a hot-melt composition that is hydrophilic. One advantage is that higher dosages of hydrophilic drugs can be employed without destroying the PSA. Another advantage is that the amount of drug released can be increased or controlled. Finally, the conditions under which a patch can be worn are greatly improved.

This invention provides a hot-melt silicone PSA composition that has improved hydrophilic characteristics while maintaining the PSA properties of shear, adhesion and release.

The instant invention introduces hot-melt PSA compositions which possess the dual benefits of being hot-melt adhesives and being formed of materials which are highly acceptable in topical applications. Our hot-melt silicone PSAs are comprised of (A) a silicone PSA selected from a mixture of (i) a silicone resin and (ii) a silicone fluid or a condensed product of (i) and (ii). This silicone PSA exhibits both tackiness and adhesiveness. Our silicone PSA is then blended with (B) from 1 to 20 weight percent, based on the total weight of (i) and (ii), of a siloxylated polyether wax. The instant invention also encompasses a method of using the composition, methods of making hot-melt silicone PSA-coated substrates and various devices made using the composition.

Component (i) of this invention is a soluble, hydroxyl-functional organopolysiloxane resin comprising  $R_3SiO_{1/2}$  siloxane units and  $SiO_{4/2}$  units, wherein R is a monovalent radical selected from hydrocarbon and halogenated hydrocarbon radicals having 1 to 20 carbon atoms. The term "soluble" means that the organopolysiloxane can be dissolved substantially completely, in either a hydrocarbon liquid such as benzene, toluene, xylene, heptane and the like or in a silicone liquid such as cyclic or linear polydiorganosiloxanes. Preferably the resin is soluble in the silicone fluid (ii).

In the formula for silicone resin (i), R denotes a monovalent radical selected from hydrocarbon and halogenated hydrocarbon radicals, preferably having less than 20 carbon atoms and most preferably having from 1 to 10 carbon atoms. Examples of suitable R radicals include alkyl radicals, such as methyl, ethyl, propyl, pentyl, octyl, undecyl and octadecyl; cycloaliphatic radicals, such as cyclohexyl; aryl radicals such as phenyl, tolyl, xylyl, benzyl, alpha-methyl styryl and 2-phenylethyl; alkenyl radicals such as vinyl; and chlorinated hydrocarbon radicals such as 3-chloropropyl dichlorophenyl and others.

To enhance the solubility of component (i) in component (ii) it is desirable to select the predominant organic radicals of the former to match the predominant organic radicals of the latter. Preferably at least one-third, and more preferably substantially all R radicals in the formula for component (i), are methyl radicals. Examples of preferred  $R_3SiO_{1/2}$  siloxane units include  $Me_3SiO_{1/2}$ ,  $PhMe_2SiO_{1/2}$  and  $Ph_2MeSiO_{1/2}$  where Me denotes methyl and Ph denotes phenyl.

It is preferred that the ratio of  $R_3SiO_{1/2}$  siloxane units to  $SiO_{4/2}$  units has a molar ratio of 0.5 to 1.2 respectively. It is further preferred that the mole ratio of the total  $R_3SiO_{1/2}$  siloxane units to  $SiO_{4/2}$  units be between 0.6 and 0.8.

Component (i) can be prepared by well known methods. It is preferably prepared by the silica hydrosol capping process of US-A 2,676,182; as modified by US-A 3,627,851 and 3,772,247. These patents teach how to prepare soluble organopolysiloxanes which are useful in the instant invention. The resulting resin can be used in our invention without further modification or it can be capped with trialkylsilyl groups to reduce the silanol content. This can be accomplished by well known methods, such as reacting the resin with a compound such as trimethylchlorosilane or hexamethyldisilazane.

Component (ii) of the instant invention is a silicone fluid, preferably a hydroxyl-terminated diorganopolysiloxane polymer. The repeat units of (ii) are  $R_2SiO_{2/2}$  siloxy units wherein R is independently selected from the same hydrocarbon and halogenated radicals defined for component (i). This component can be comprised of a single polymer or copolymer or it can be a mixture of two or more of such polymers.

For the present invention, each polydiorganosiloxane polymer should have a viscosity at 25 °C. of 100 to 500,000 mPa·s [centipoise (cP)], preferably 500 to 50,000 and most preferably 1,000 to 20,000 mPa·s. It is preferred that at least 50%, and preferably at least 85%, of the organic radicals along the chain of component (ii) are methyl radicals, which can be distributed in any manner in the diorganopolysiloxane.

5 Further, component (ii) can comprise up to 10 mole percent of siloxane branching sites provided it meets the viscosity requirements.

The silicone resin (i) is employed in amount from about 40 to 70 parts by weight in the silicone PSA and the silicone fluid (ii) is employed from 30 to 60 parts by weight, wherein the total parts of the silicone resin and the silicone fluid are 100 parts. It is usually preferred that the silicone resin be employed from 50  
10 to 60 parts by weight, and correspondingly, that the silicone fluid be employed from 40 to 50 parts by weight, wherein the total parts by weight equals 100.

Additionally, the silicone PSA which is mixed with the siloxylated polyether wax may be selected from various known silicone PSAs which may or may not be condensed products of (i) and (ii). The hot-melt silicone PSA of the instant invention do not employ solvents that are found in traditional PSAs.

15 One suitable class of PSAs employed in the hot-melt composition of our invention consists of a mixture of (i) a trimethylsilyl-endblocked polysilicate resin and (ii) a silicone fluid. Component (i) is a silicone resin consisting of a benzene-soluble resinous copolymer containing silicon-bonded hydroxyl radicals and consisting essentially of triorganosiloxy units of the formula  $R^1_3SiO_{1/2}$  and tetrafunctional siloxy units of the formula  $SiO_{4/2}$  in a ratio of 0.6 to 0.9 triorganosiloxy units for each tetrafunctional siloxy unit present in the  
20 copolymer.  $R^1$  therein is a monovalent organic radical independently selected from the group consisting of hydrocarbon radicals of from 1 to 6 carbon atoms. Component (ii) is a silanol-endcapped polydiorganosiloxane fluid such as a polydimethylsiloxane fluid. Representative PSA compositions of this type are taught in US-As 2,736,721 and 2,814,601.

Another class of suitable PSAs for use according to the invention is described in US-A 2,857,356. It  
25 discloses a silicone PSA which consists of a mixture of ingredients comprising (i) a cohydrolysis product of a trialkyl hydrolyzable silane and alkyl silicate, wherein the cohydrolysis product contains a plurality of silicon-bonded hydroxy groups and (ii) a linear, high viscosity organopolysiloxane fluid containing silicon-bonded hydroxy groups.

The silicone resin (i) and the silicone fluid (ii) may optionally be condensed together according to a  
30 procedure described in CA-A 711,756. In the condensation reaction, the silicone resin (i) and silicone fluid (ii) are mixed together in the presence of a catalytic amount of a silanol condensation catalyst and then (i) and (ii) are condensed by heating under reflux conditions for 1 to 20 hours. Examples of silanol condensation catalyst are primary, secondary and tertiary amines, carboxylic acids of these amines and quaternary ammonium salts.

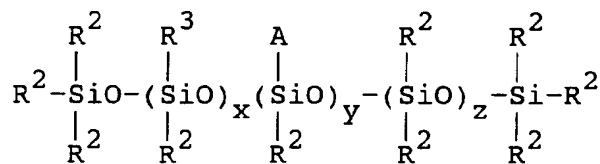
35 Another class of suitable PSAs for use with our siloxylated polyether waxes are those compositions described in US-As 4,591,622; 4,584,355; 4,585,836 and 4,655,767. Generally, these PSAs consist of a blend of (i) a silicone resin and (ii) a silicone fluid which are chemically treated to reduce the silicon-bonded hydroxyl content of the blend. These adhesives may optionally be condensed, as described previously, prior to chemical treatment.

40 The silicone PSAs useful in this invention should not be confused with silicone rubbers which are not satisfactorily useful. The silicone PSAs are usually fillerless or contain low amounts of less than 5% of fillers. Contrastingly, silicone rubbers typically contain from 15 to 35 percent filler. Fillers are generally not required in high quantities in silicone PSAs because high quantities of filler often cause the silicone PSAs to lose tack and adhesiveness or to increase in dynamic viscosity, making it more difficult to apply a coating  
45 of the silicone PSA.

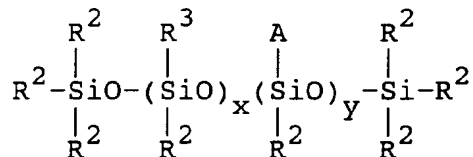
Component (B) of the instant invention is a siloxylated polyether wax. Generally, any silicone polymer that contains both an alkyl wax ( $\geq C_6$ ) functionality and a polyethylene oxide functionality will be useful in our invention. Our siloxylated polyether waxes (B) are exemplified by silicone polymers having the general formula

50

55



and



wherein each  $R^2$  is independently selected from an alkyl radical having 1 to 4 carbon atoms, a phenyl radical and a hydroxyl radical;  $R^3$  is an alkyl radical having 6 or more carbon atoms; A is a polyethylene oxide group selected from  $-R^4O(CH_2CH_2O)_aR^5$  or  $-R^4O(CH_2CH_2O)_a(CH_2(CH_3)CHO)_bR^5$  where  $R^4$  is an alkylene radical having from 1 to 6 carbon atoms;  $R^5$  is selected from -H or  $-COCH_3$ ;  $a$  has a value of at least 1 and  $b$  has a value of at least 1,  $x$  has a value of greater than 0;  $y$  has a value of greater than 0; and  $z$  has a value of 1 to 100.

In the formulas for the siloxylated polyether waxes (B),  $R^2$  is selected from an alkyl radical having 1 to 4 carbon atoms, a phenyl radical and a hydroxyl radical. Examples of suitable  $R^2$  radicals are methyl, ethyl, phenyl and hydroxyl. Preferably at least 90 mole percent of the  $R^2$  radicals are methyl and more preferably all of the  $R^2$  radicals are methyl.

$R^3$  in the siloxylated polyether wax is selected from alkyl radicals having 6 or more carbon atoms. Examples of  $R^3$  are hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, tetracosyl and triacontyl.

"A" in the siloxylated polyether wax formula is a polyethylene oxide group selected from  $-R^4O(CH_2CH_2O)_aR^5$  or  $-R^4O(CH_2CH_2O)_a(CH_2(CH_3)CHO)_bR^5$  where  $R^4$  is an alkylene radical having from 1 to 6 carbon atoms;  $R^5$  is selected from -H or  $-COCH_3$ ;  $a$  has a value of at least 1, preferably at least 20; and  $b$  has a value of at least 1. It is generally recognized in the art that the presence of polypropylene oxide groups can be detrimental to hydrophilicity. Therefore, it is further preferred that when "A" is the group  $-R^4O(CH_2CH_2O)_a(CH_2(CH_3)CHO)_bR^5$  that  $b$  has a value of 1 to 20 and that  $a+b \geq 50$ . One skilled in the art will readily determine the amount of polypropylene oxide that can be present without losing the hydrophilic characteristics of the wax.  $R^4$  is exemplified by methylene, ethylene, propylene, butylene and others.

In the preceding siloxylated polyether wax formulas,  $x$  has a value of greater than 0, preferably 1 to 70;  $y$  has a value of greater than 0, preferably 1 to 70; and  $z$  has a value of 1 to 400, preferably 1 to 100.

The polymeric structure of our siloxylated polyether waxes is not specifically limited; however, these waxes should be selected such that the melting point is greater than  $37^\circ\text{C}$ . but less than  $200^\circ\text{C}$ . Preferably our siloxylated polyether waxes should have a melting point of between  $50^\circ\text{C}$  and  $150^\circ\text{C}$ . Siloxylated polyether waxes useful in the instant invention are generally known in the art.

The siloxylated polyether wax (B) is employed in an amount of 1 to 20 weight percent, preferably from 5 to 15 weight percent, based on the total weights of the silicone resin (i) and the silicone fluid (ii).

The siloxylated polyether wax functions to decrease the dynamic viscosity of our hot-melt PSA at temperatures equal to or less than  $200^\circ\text{C}$ . Desirable dynamic viscosities of our wax-containing adhesives at temperatures equal to or less than  $200^\circ\text{C}$ . are equal to or less than  $80\text{ Pa}\cdot\text{s}$  (800 poise).

Small amounts of additional ingredients may also be added to the compositions of this invention. For example, antioxidants, pigments, stabilizers, fillers and others may be added as long as they do not materially alter the requirements of the desired composition. If our hot-melt silicone PSA compositions contain a filler, it is desired that the filler be present in an amount of no greater than 5 weight percent based on the total weight of the silicone resin and silicone fluid.

Additionally, hot-melt PSA additives known in the art, which are effective at reducing dynamic viscosity, such as the esters described in US-A 4,865,920; the polyphenylsiloxane fluids described in US-A 5,162,410, the non-flammable hydrocarbons described in EP-A 0 443 759 and others, may be incorporated into our hot-melt silicone PSA compositions.

Our hot-melt silicone PSA compositions are prepared by merely mixing the silicone PSA comprised of siloxanes (i) and (ii) with the selected siloxylated polyether wax. This hot-melt silicone PSA is then heated to

a coatable viscosity and coated on a substrate. Optionally the coated compositions may be cured. When our composition is to be cured, the composition may further contain a curing catalyst. It is preferred that such catalysts remain inactive at room temperature and at temperatures reached during the hot-melt coating process. Therefore, catalysts that either become active at temperatures higher than that of the hot-melt temperatures or become active upon exposure to another energy source such as UV light or electron beam radiation, are most suitable. The amount of catalyst employed should be sufficient to accelerate the cure of the composition. This amount can be readily determined by one skilled in the art through routine experimentation and is typically 0.1 to 1.0 percent based on the weight of the total composition.

When using our hot-melt silicone PSA compositions to coat a substrate, our method comprises the steps of (a) heating the hot-melt silicone PSA composition to a coatable temperature above 25 °C., (b) coating the heated hot-melt silicone PSA composition onto the substrate and (c) cooling the coated hot-melt silicone PSA until it is in a generally non-flowing state. Typically, heating the hot-melt silicone PSA compositions of the instant invention to temperatures above 100 °C., preferably 150 °C., results in viscosities suitable for coating. These coatable temperatures are low enough so that decomposition of the PSA composition does not occur. Lower temperatures may result in coatable viscosities depending on the coating equipment used, the desired end-product and the formulation of the hot-melt silicone PSA composition. For example, the thicker the layer of PSA desired, the higher the coating viscosity can be.

When the hot-melt silicone PSA compositions of this invention are applied to a backing or substrate, this procedure may be accomplished by using any conventional means, such as roller coating, dip coating, extrusion, knife coating or spray coating.

The hot-melt silicone PSA compositions of the present invention will adhere to many substrates, such as paper, cloth, glass cloth, silicone rubber, polyethylene, polyethylene terephthalate, polytetrafluoroethylene, glass, wood, metals and skin. Therefore, there are many uses for the hot-melt silicone PSA compositions of the instant invention. Depending on the desired use, it may be desirable to apply adhesion promoters on the substrate surface upon which the hot-melt silicone PSA compositions will be placed.

The hot-melt silicone PSA compositions of our invention are especially suitable for assisting in delivery of a bioactive agent, such as a drug to a bioactive agent-accepting substrate, such as a patient's skin. Our hot-melt silicone PSA compositions may be employed in several types of bioactive agent delivery modes. One mode incorporates the bioactive agent into the hot-melt silicone PSA composition on an impermeable backing which is thereafter attached to the bioactive agent-accepting substrate to commence delivery. A second mode attaches a permeable membrane of material to the bioactive-agent accepting substrate using our hot-melt silicone PSA composition and then, contacting a reservoir of a bioactive agent to the attached permeable membrane.

The bioactive agent may then pass from the reservoir through the permeable membrane and to the substrate for absorption. For this mode, a bioactive agent delivery device may be made which includes (a) a container, (b) a bioactive agent contained in the container and (c) our hot-melt silicone PSA composition on the container for providing a means for adhering the container to the bioactive agent-accepting substrate. Another mode of delivery comprises either the first or second mode; however, the adhesive is placed on the impermeable backing or the permeable membrane along the outside perimeter of either the backing or membrane.

Due to the presence of siloxylated polyether waxes in our hot-melt silicone PSA composition, the resulting adhesives have improved hydrophilic characteristics, thus allowing quicker delivery of drugs that are hydrophilic in nature. Further, our use of siloxylated polyether waxes reduces the dynamic viscosity of the PSA which improves the coatability of hot-melt silicone PSAs at temperatures at or below 200 °C.

So that those skilled in the art can understand and appreciate the invention taught herein, the following examples are presented.

In the following examples:

RESIN A is a xylene solution of a resinous copolymeric siloxane prepared from 45 parts of sodium silicate and 20 parts  $(\text{CH}_3)_3\text{SiCl}$  according to the method of US-A 2,676,182. Resin A and contains  $\text{Me}_3\text{SiO}_{1/2}$  units and  $\text{SiO}_{4/2}$  units in a ratio of approximately 0.75:1.0, has a nonvolatile content (NVC) of typically 69 to 71%, an acid number in the range of 0.3 to 1.4, a viscosity of 90 mm<sup>2</sup>/s (cSt) at 25 °C. and a silicon-bonded hydroxyl content of 2.5 weight percent at 100% NVC.

FLUID A is a hydroxyl-endblocked polydimethylsiloxane fluid having a viscosity of 13,500 mPa·s (cP) at 25 °C.

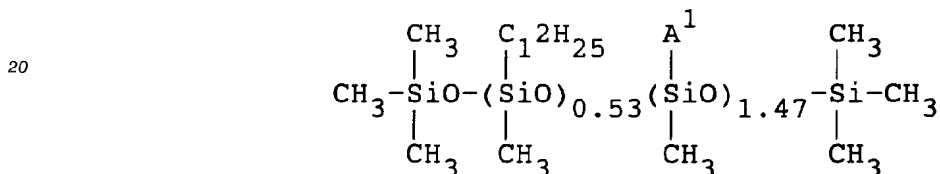
PSA 1 was prepared by mixing 27.2 parts Fluid A, 47.5 parts Resin A and 11.6 parts xylene. The mixture was heated to 115 °C. and anhydrous ammonia was passed through the mixture to promote silanol condensation. Water produced from the condensation was continuously driven off until the desired viscosity

was attained. The ammonia was then discontinued. 13.6 parts of hexamethyldisilazane were then added to cap the residual silanol and to render the product non-reactive. The resulting product was stripped and devolatilized to 99% NVC to form the PSA.

PSA 2 was prepared by mixing 15.7 parts Fluid A, 31.1 parts Resin A and 6.7 parts xylene. The mixture was heated to 115°C. and anhydrous ammonia was passed through the mixture to promote silanol condensation. Water produced from the condensation was continuously driven off until the desired viscosity was attained. The ammonia was then discontinued. Nine (9.0) parts of hexamethyldisilazane were then added to cap the residual silanol and to render the product non-reactive. The resulting product was stripped to remove volatiles. 15 weight parts of 1,000 mm<sup>2</sup>/s (cSt) polydimethylsiloxane fluid were then added to produce the PSA.

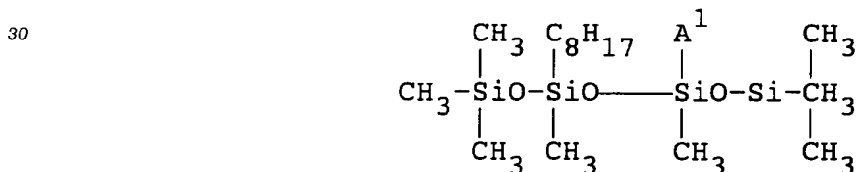
PSA 3 was prepared by mixing 31.5 parts Fluid A, 55 parts Resin A and 13.5 parts xylene. The mixture was heated to 115°C. and anhydrous ammonia was passed through the mixture to promote silanol condensation. Water produced from the condensation was continuously driven off until the desired viscosity was attained. The ammonia was then discontinued. 7 weight parts of 100 mm<sup>2</sup>/s (cSt) polydimethylsiloxane fluid were then added. The resulting product was stripped to remove volatiles to 99% NVC.

WAX 1 is a siloxylated polyether wax having the formula



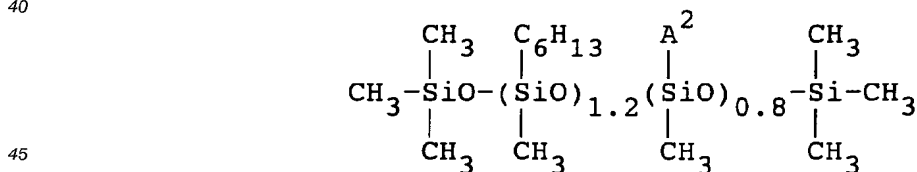
where A<sup>1</sup> is -(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>32</sub>COCH<sub>3</sub>. Wax 1 has a melting point of 45°C.

WAX 2 is a siloxylated polyether wax having the formula



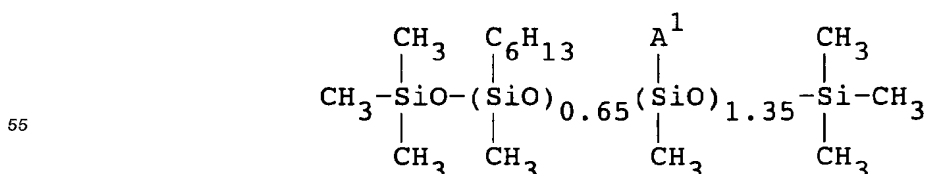
where A<sup>1</sup> is -(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>32</sub>COCH<sub>3</sub>. Wax 2 has a melting point of 37°C.

WAX 3 is a siloxylated polyether wax having the formula



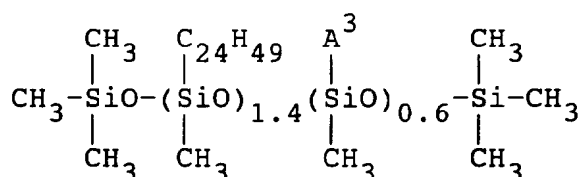
where A<sup>2</sup> is -(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>24</sub>COCH<sub>3</sub>. Wax 3 has a melting point of 36°C.

WAX 4 is a siloxylated polyether wax having the formula



where A<sup>1</sup> is  $-(CH_2)_3O(CH_2CH_2O)_{32}COCH_3$ . Wax 4 has a melting point of 43 °C.

WAX 5 is a siloxylated polyether wax having the formula



where A<sup>3</sup> is  $-(CH_2)_3O(CH_2CH_2O)_{100}COCH_3$ . Wax 5 has a melting point of 55 °C.

The physical properties of release, adhesion and shear were measured on the hot-melt silicone PSAs. Measurements were obtained by testing a 25.4 mm (one inch) wide polyester tape having a silicone PSA thereon. The hot-melt silicone PSAs of our invention were cast to yield a 0.05 mm (2 mil) thickness dry adhesive on "SCOTCH-PAK"™ 1022 Release liner, a polyester film coated with a release coating available from 3M Company, St. Paul, Minnesota. After coating, a "MYLAR"™ polyester film was adhered to each casted sample with a 2.04 kg (4.5 lb) rubber transfer roller.

The laminate was then cut into 25.4 mm (one-inch) wide strips with the use of a 25.4 mm (one-inch) tape specimen cutter received from the Pressure Sensitive Tape Council. The following properties were then measured: RELEASE: The release values were obtained by stripping the tape from the SCOTCH-PAK 1022 Release Liner at a rate of 101.6 cm/min (40 inches/minute) at an angle of 180 ° while attached to a tensile testing machine. An average value over the entire length of the liner was recorded. Release values of less than 50 gm/cm are considered acceptable. ADHESION: The adhesion values were obtained as follows. The tapes having the silicone PSA composition thereon were adhered to a stainless steel panel with a 2.04 kg (4.5 lb) roller and allowed to rest for 20 minutes. The adhesion measurements were obtained by stripping each tape from the panel at a rate of 30.5 cm/min (12 inches/minute) at an angle of 180 ° while attached to a tensile testing machine. Desirable values range between 100 and 2000 gm/cm. SHEAR: Shear values were measured by cutting three strips of the prepared laminates 2.5 cm wide and 7.5 cm in length. A 3.5 cm wide by 5.0 cm long strip of MYLAR™ was applied to the adhesive strip to provide an overlap of 2.5 cm in a lengthwise direction. These were laminated using a 2.04 kg (4.5 lb) roller and allowed to equilibrate for 20 minutes. The specimen was mounted in the jaws of an Instron™ Model 1122 Tensometer, available from Instron Corporation and pulled at a speed of 0.5 cm/min. The peak load required to shear and separate the laminate was recorded in kg/6.25 cm<sup>2</sup>. Desirable values range between 4 and 25 kg/6.25 cm<sup>2</sup>. WATER SWELL: 5 to 7 gram samples of the adhesive were hot pressed between release liner to yield a dry adhesive film of 3.3 mm (0.130 inch) thickness at 125 °C. Once cooled, the samples were weighed and placed in a petri dish lined with release liner. The samples were then covered with distilled water for 24 hours. The samples were removed and air-blown dried to remove surface water. The samples were then weighed again to determine the water weight gain. The samples were then returned to the water and the procedure repeated at 48 hours. A positive water weight gain is desired.

DYNAMIC VISCOSITY (n\*), ELASTIC STORAGE MODULI (G') and FLUID LOSS MODULI (G''): The dynamic viscosity, elastic storage moduli and fluid loss moduli were measured on the adhesive compositions using a Rheometrics™ Dynamic Spectrometer, Model RDS2, available from Rheometrics, Piscataway NJ. A temperature sweep was run on 4 gram samples of 1 mm thickness and the tester was operated at a frequency of 100 radians/sec, at a 1% strain using a 50 mm cup and plate. Desirable dynamic viscosities (n\*) should be less than or equal to 80 Pa·s (800 poise) at or below 200 °C. ELASTIC STORAGE MODULI (G'): Elastic storage modulus is related to die swell and elastic memory. The higher the die swell, the smaller the size of an orifice required for a given coating thickness. Therefore, the lower the elastic storage modulus, the better, as it is then easier to coat onto a substrate. Tests similar to those run in these examples are described in ASTM 4065-82. Desirable storage modulus values should be less than 45,000 dynes/cm<sup>2</sup> at or below 200 °C.

#### EXAMPLES 1-10

In Examples 1-5, 7 and 9 the hot-melt silicone PSA compositions were prepared by mixing the compositions indicated in Table 1 at 100 °C until homogeneously mixed and then allowing the mixture to cool to room temperature. Examples 6, 8 and 10 are provided to show the properties of the various silicone PSAs without the siloxylated polyether waxes.

TABLE 1

Example #	PSA Type Employed	Wax Employed	Weight % Wax*
1	1	1	10%
2	1	2	10%
3	1	3	10%
4	1	4	10%
5	1	5	10%
6	1	none	0%
7	2	5	10%
8	2	none	0%
9	3	5	10%
10	3	none	0%

\*Based on the total weight of the silicone fluid and silicone resin in the PSA composition.

As shown in Table 2, these adhesives were evaluated for physical properties of release (g/cm), adhesion (g/cm), shear (kg/6.25cm<sup>2</sup>) and water swell (%). Release values ranged between 4 and 24 g/cm and all samples were within the acceptable range of less than or equal to 50 gm/cm. Adhesion values ranged between 0 and 350 g/cm and samples 4, 5, 7 and 9 were within the acceptable range of 100-2,000 gm/cm. Shear values ranged from 0 to 11.6 Kg/2.5cm<sup>2</sup> and samples 5 and 7 were within the acceptable range of 5 to 25 kg/6.25 cm<sup>2</sup>. All of the samples showed a positive water swell which indicates that the PSA's are hydrophilic in nature. These results show that the addition of siloxylated polyether waxes to our PSAs do not adversely affect the physical properties of the PSAs.

TABLE 2

Example #	Release g/cm	Adhesion g/cm	Shear kg 6.25 cm <sup>2</sup>	Water Swell %	
				24hrs	48hrs
1	14	23	0.7	2.4	2.8
2	10	0	0.0	1.4	2.0
3	25	3	0.7	1.6	2.3
4	4	299	4.1	1.4	2.4
5	7	347	11.6	1.9	2.7
6	4	597	13.5	--	0.4
7	6	184	5.0	1.2	1.9
8	16	206	8.0	0.03	0.15
9	5	331	3.0	3.3	4.4
10	13	310	4.5	0.04	0.2

Results of dynamic viscosity, elastic storage moduli and fluid loss moduli are given in Table 3. Decreased dynamic viscosity values are desirable to improve coatability without solvents. Each sample containing our siloxylated polyether wax demonstrated the desirable decreasing dynamic viscosity in comparison to the control PSA.



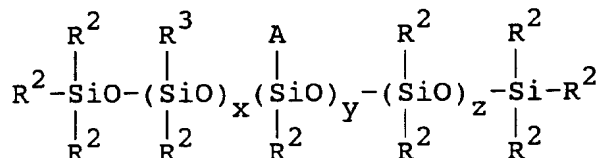
TABLE 3

Example #	50 ° C			200 ° C		
	G'	G''	N*	G'	G''	N*
1	640,000	180,000	6,600	33,000	44,000	550
2	640,000	190,000	6,600	37,000	49,000	620
3	630,000	190,000	6,600	31,000	42,000	510
4	670,000	180,000	6,900	20,000	28,000	350
5	560,000	210,000	5,900	25,000	35,000	460
6	702,500	148,800	7,180	84,500	92,400	1250
7	480,000	1,000,000	12,000	7,800	17,000	190
8	550,000	1,500,000	16,000	12,000	29,000	310
9	*	*	*	*	*	*
10	340,000	490,000	66,000	6,000	18,000	190

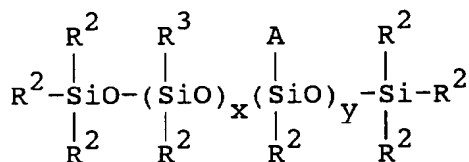
\* Unable to compress material between plates to 1mm gap, no test run.

## Claims

1. A hot-melt silicone pressure sensitive adhesive composition, comprising (A) a silicone pressure sensitive adhesive selected from a mixture of (i) a silicone resin and (ii) a silicone fluid or a condensed product of (i) and (ii); the silicone pressure sensitive adhesive exhibiting tackiness and adhesiveness; and (B) from 1 to 20 weight percent, based on the total weight of (i) and (ii) of a siloxylated polyether wax selected from waxes having the following formula:



and



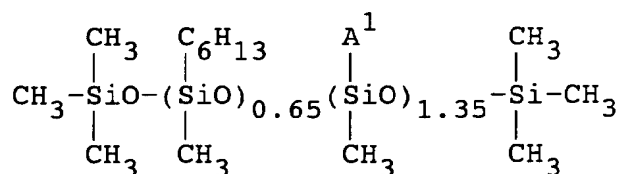
wherein each  $R^2$  is selected from an alkyl radical having 1 to 4 carbon atoms, a phenyl radical and a hydroxyl radical;

$R^3$  is an alkyl radical having 6 or more carbon atoms;

A is a polyethylene oxide group selected from  $-R^4O(CH_2CH_2O)_aR^5$  or  $-R^4O(CH_2CH_2O)_a(CH_2(CH_3)-CHO)_bR^5$  where  $R^4$  is an alkylene radical having from 1 to 6 carbon atoms,  $R^5$  is selected from  $-H$  and  $-COCH_3$ ,  $a$  has a value of at least 1 and  $b$  has a value of at least 1;

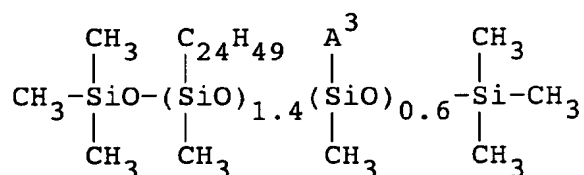
$x$  has a value of greater than 0;  $y$  has a value of greater than 0; and  $z$  has a value of 1 to 100; and wherein the siloxylated waxes have a melting point of from 37 ° C. to 200 ° C.

2. The adhesive composition as claimed in claim 1 wherein the siloxylated polyether wax is



where A<sup>1</sup> is -(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>32</sub>COCH<sub>3</sub>.

3. The adhesive composition as claimed in claim 1 wherein the siloxylated polyether wax is



where A<sup>3</sup> is -(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>100</sub>COCH<sub>3</sub>.

4. The adhesive composition as claimed in claim 1 wherein the silicone resin is a hydroxyl-functional organopolysiloxane resin comprising R<sub>3</sub>SiO<sub>1/2</sub> siloxane units and SiO<sub>4/2</sub> units, wherein R is a monovalent radical selected from hydrocarbon or halogenated hydrocarbon radicals having 1 to 20 carbon atoms.
5. The adhesive composition as claimed in claim 4 wherein the hydroxyl-functional organopolysiloxane resin has a mole ratio of the total R<sub>3</sub>SiO<sub>1/2</sub> siloxane units to SiO<sub>4/2</sub> units of 0.5 to 1.2.
6. The adhesive composition as claimed in claim 1 wherein the silicone fluid is a hydroxyl-terminated diorganopolysiloxane polymer containing repeat units of R<sub>2</sub>SiO<sub>2/2</sub> siloxy units wherein R is a monovalent radical selected from hydrocarbon or halogenated hydrocarbon radicals having 1 to 20 carbon atoms.
7. The hot-melt silicone pressure sensitive adhesive as claimed in claim 1, further comprising a bioactive agent.